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PURDUE MATERIALS ENGINEERING

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# Effect of Biofuel Impurities On The Hot Corrosion of Yttria-Stabilized Zirconia Thermal Barrier Coatings

PURDUE CHEMISTRY

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# Constituents Of CMAS And Its Effect On TBC's

Persian Gulf War: U.S. Navy F-14A Tomcat. [1]

Eyjafjallajokull ash cloud April 17, 2010. [2]

**Sources of Contaminants**

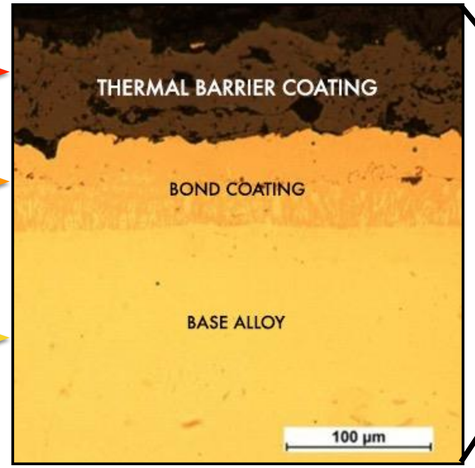
- Middle East Sand
- Volcanic Ash

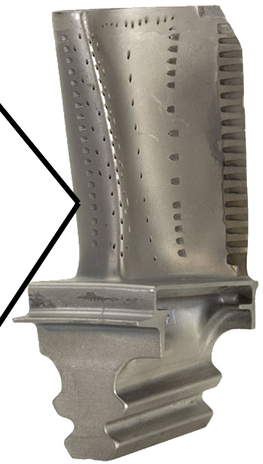
CMAS ($CaO$-$MgO$-$Al_2O_3$-$SiO_2$) $T_m$~1250ºC

**93%$ZrO_2$ -7%$Y_2O_3$ (YSZ)**

**CoNiCrAlY**

**Hastalloy-X**



***Thermal Barrier Coating (TBC)***

- Essential coating in any gas turbine
- CMAS is highly detrimental for the TBC

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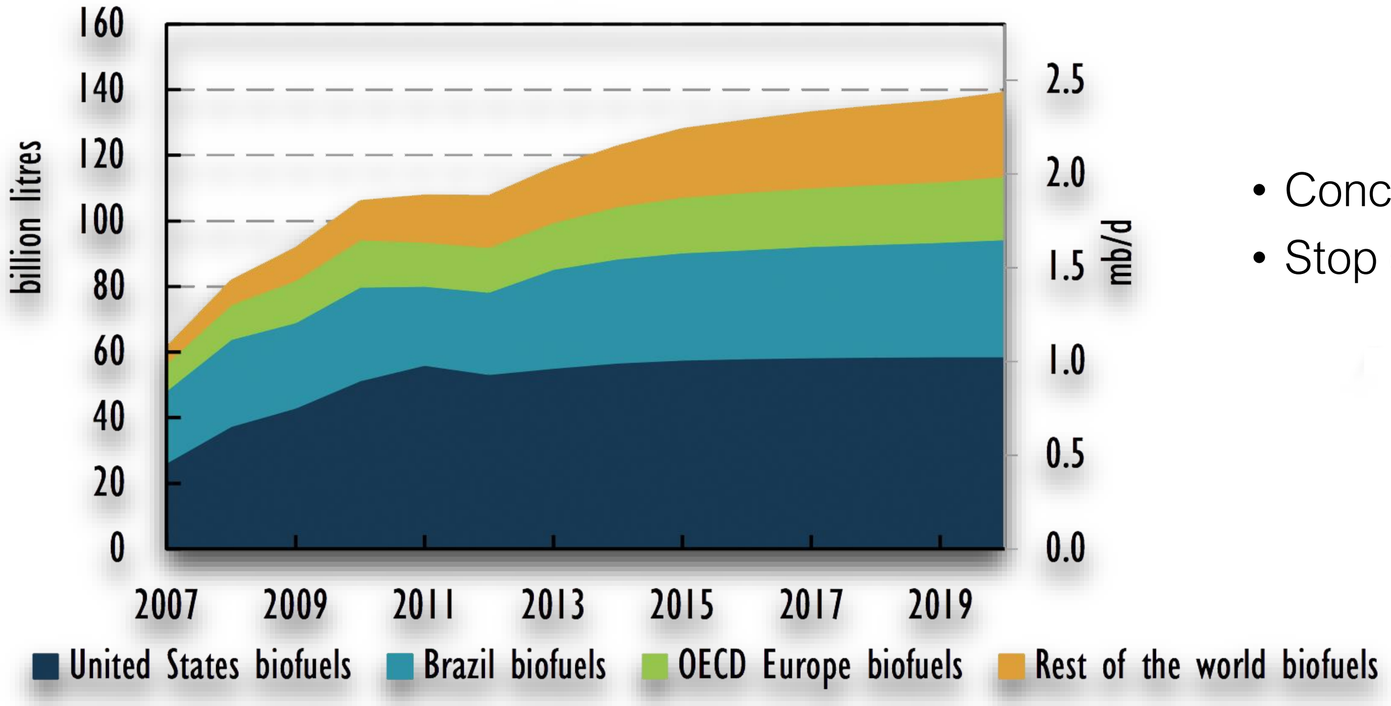
1.- Encyclopedia Britannica Online, Retrieved October 19, 2016
2.- Matthew J. Roberts , Eyjafjallajokull ash cloud, April 17, 2010

# The Present And The Future Of Biofuels Worldwide




**Why do we need biofuels?**

- Concerns about fossil fuels reliability.
- Stop global warming and green house gas emissions

**Jet A** – Petroleum Fuel
**HEFA** – Hydroprocessed Esters and Fatid Acids
**FT-S8** – Fischer-Tropsch
**SIP** – Synthesized Isoparaffin


**A commercial aircraft (left picture) and a military F-18 (right picture) being tested for the use of Biofuels. blends.** [3]

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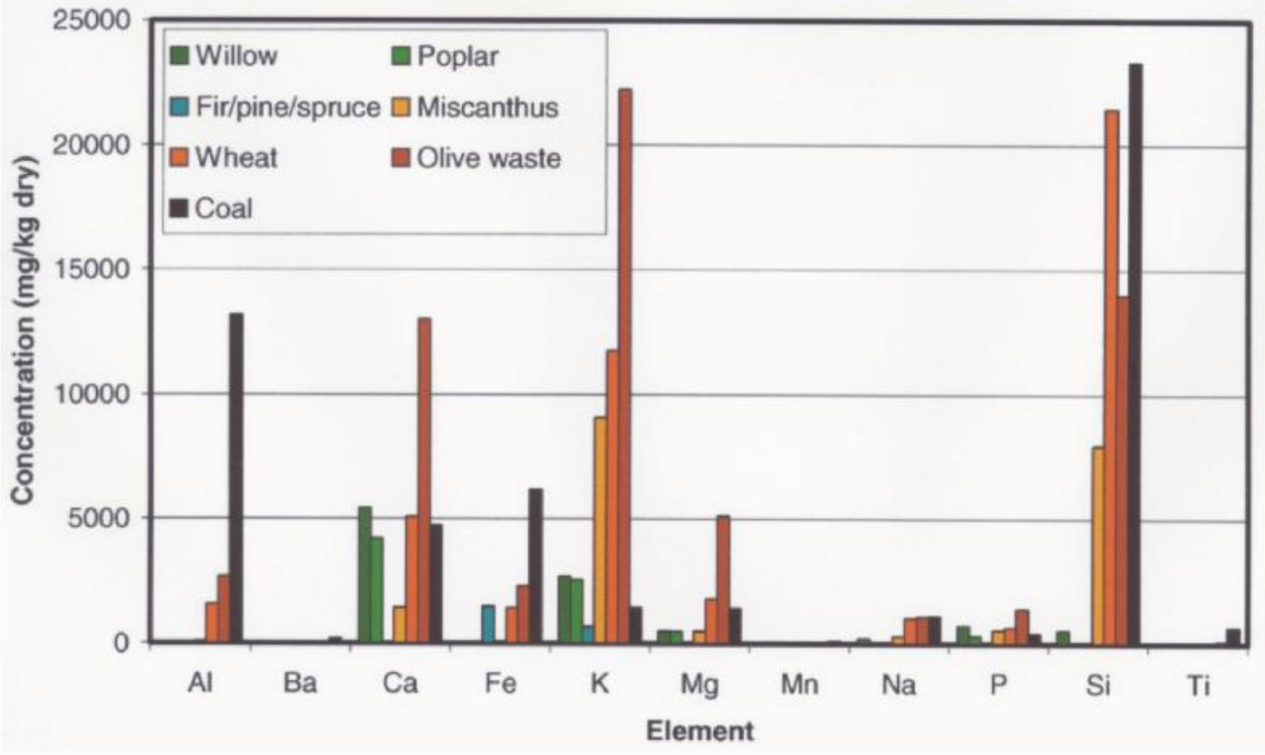
3.- G. Koçar and N. Civaş, "An overview of biofuels from energy crops: Current status and future prospects," Renew. Sustain. Energy Rev., 28 900–916 (2013).

# Individual Constituents Of CMAS Found In Biofuels




**Selected minor and trace elements present in a range of different biomass (Simms et al., 2007b)[6]**

- In biomass, the alkali metals are mostly present in a different chemical form than for coals (Livingston, 2009)[4], and so are much more readily released during combustion.

- There is also a different balance between the alkali metals, with much more K than Na; as with Cl, higher K levels are found in faster growing biomass (Simms et al., 2007a)[5].

- Alkaline Metals (Na,K,Ca, Mg)
- Si, Al, S (Generally Alone)

CMAS ($CaO$-$MgO$-$Al_2O_3$-$SiO_2$)

**Factors that affect the composition of Biomass**

- Composition of the soil.
- Drying Temperature
- Harvest Season


4. Livingston W R (2009), 'Fouling corrosion and erosion', in Bridgwater A V, Hofbauer H and van Loo S (eds), Thermal Biomass Conversion, CPL Press, pp. 157–176.
5. Simms N J, Kilgallon P J and Oakey J E (2007a), 'Energy Materials: Materials Science and Engineering for Energy Systems, 2, 154–160.
6. Simms N J, Kilgallon P J and Oakey J E (2007b), 'Degradation of heat exchanger materials under biomass co-firing conditions', Materials at High Temperatures, 24, 333–342.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# Experimental Methodology

**Different Sample Types**

- Air Plasma Spray **(APS)** and Electron Beam Physical Vapor Deposition **(EB-PVD)** samples.

Solutions of multiple types of impurities.


**Impurity Cocktail**

**Deposition of Impurities**

Apply different concentrations of impurities over the TBC's.

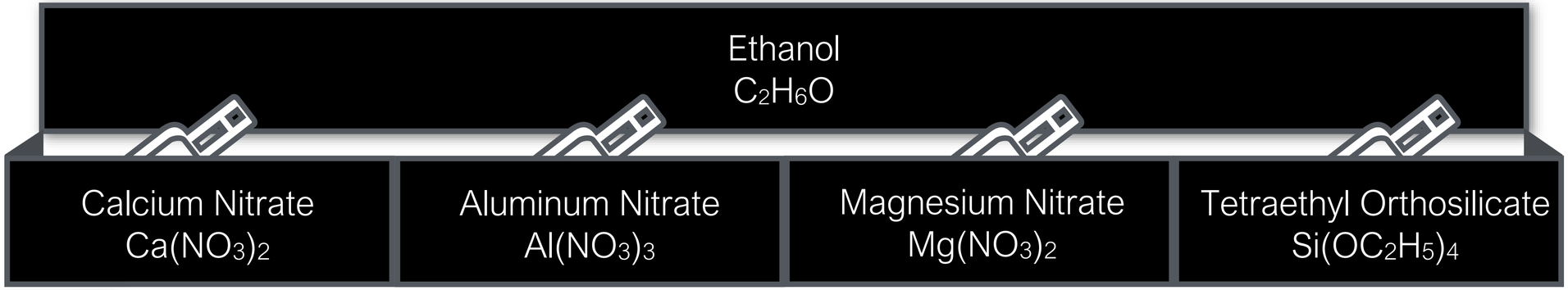
- Cycle Test: 10x to 100x.
- Fast Cycles: 2 to 5 min.
- High Temp Cycles: 25ºC -1300 C.

**Ablation Rig**

**Scanning Electron Microscopy**

- Evaluate microstructure.
- Identify secondary phases.
- Study oxidation products.

# Incorporation Of Biofuels Impurities In a Single Solution (Impurity Cocktail)





- A single solution containing the individual constituents of biofuel Impurities.
- No precipitation or segregation is observed in the solution of impurities.
- Instead of burning thousands of gallons of fuels, we can test a single solution with the necessary composition and concentration.

- A test of a single solution instead of burning thousands of gallons of fuel.
- Concentration/composition of **"cocktail"** are versatile.

CMAS ($CaO$-$MgO$-$Al_2O_3$-$SiO_2$)

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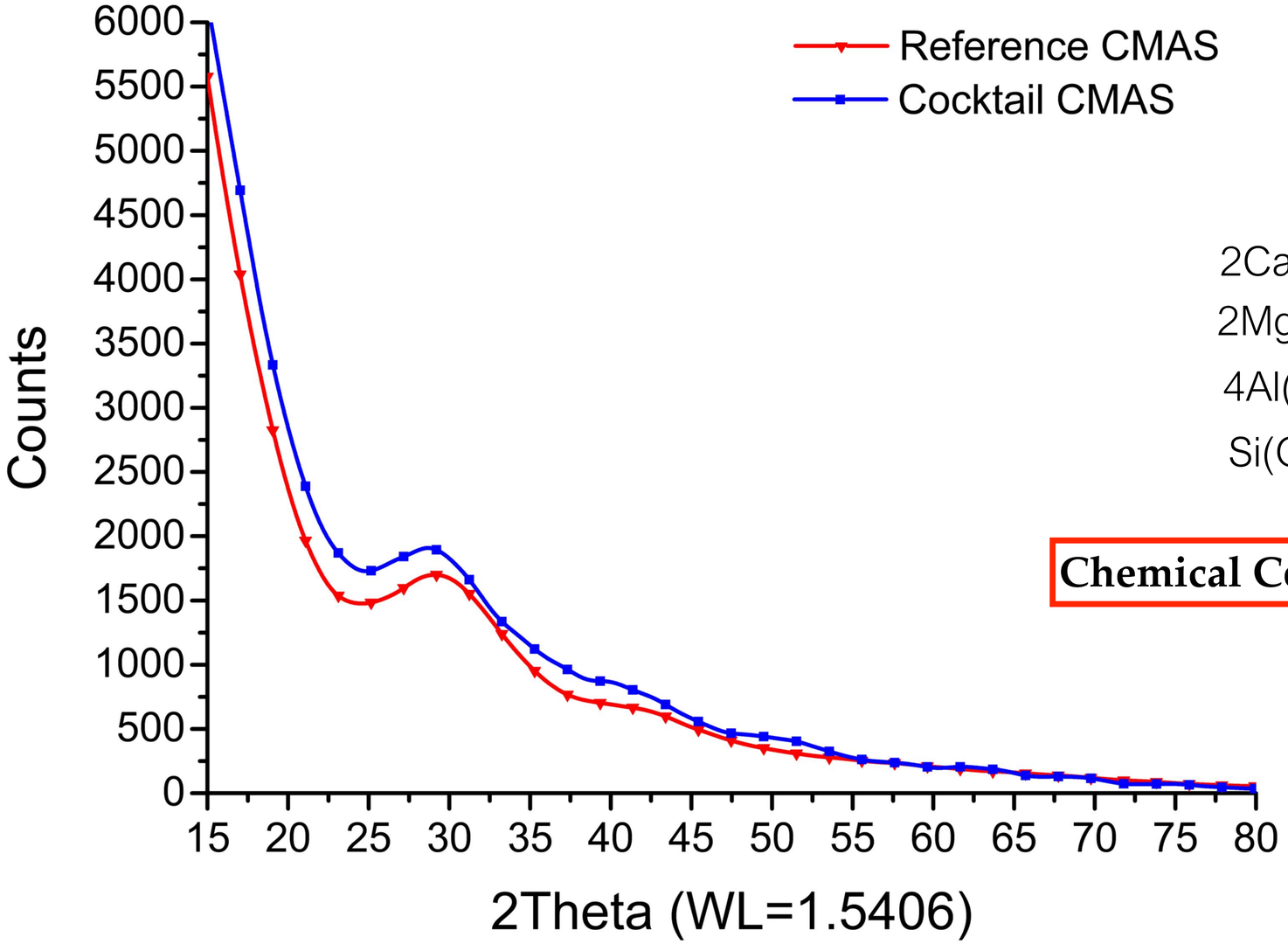
# X-Ray Diffraction (XRD) Of CMAS And (Impurity Cocktail)




$$2Ca(NO_3)_2 \longrightarrow \mathbf{2CaO} + 4NO_2 + O_2$$

$$2Mg(NO_3)_2 \longrightarrow \mathbf{2MgO} + 4NO_2 + O_2$$

$$4Al(NO_3)_3 \longrightarrow \mathbf{2Al_2O_3} + 12NO_2 + 3O_2$$

$$Si(OC_2H_5)_4 \longrightarrow \mathbf{SiO_2} + 2C_2H_3OH + 2C_2H_4$$

**Chemical Composition: $27.8CaO - 4MgO - 5Al_2O_3 - 61.6SiO_2$**


7. G. Pujol, F. Ansart, J.P. Bonino, A. Malié, and S. Hamadi, “Step-by-step investigation of degradation mechanisms induced by CMAS attack on YSZ materials for TBC applications,” Surf. Coatings Technol., 237 71–78 (2013).

8. N.P. Bansal and S.R. Choi, “Properties of CMAS glass from desert sand,” Ceram. Int., 41 [3] 3901–3909 (2015).

9. C. Mgo, A.O. Sio, C. Deposits, J. Yang, C.G. Levi, and C.A. Johnson, “Thermochemical Interaction of Thermal Barrier Coatings with Molten,” 3175 3167–3175 (2006).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# Deposition Of Biofuel Impurities Over The TBC

Clamp

Spray Gun &Cocktail

Sample

Hot Plate


C

M

A

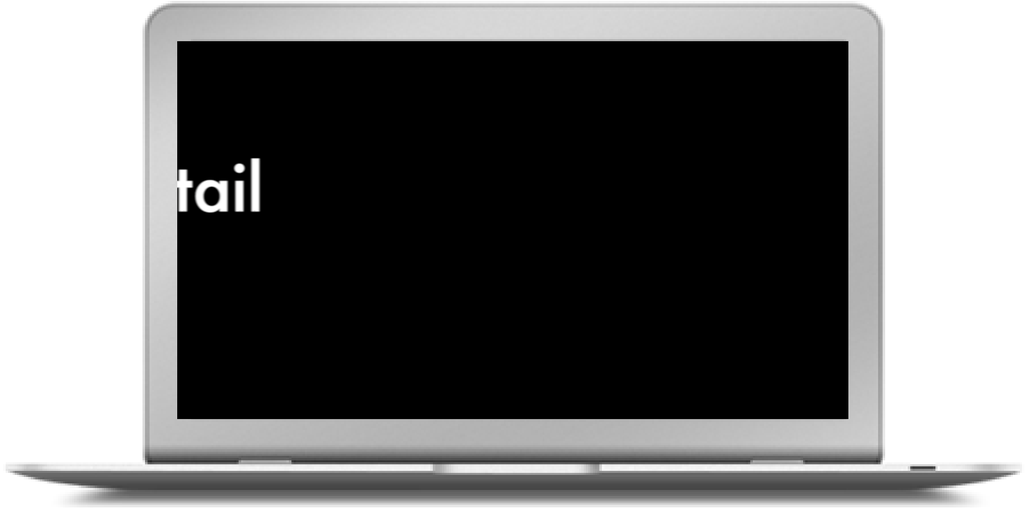
S


$Ca(NO_3)_2$ 27%

$Mg(NO_3)_2$ 4%

$Al(NO_3)_3$ 16%

$Si(OC_2H_5)_4$ 53%




- Minimum mesurable concentration 0.001 mg/in$^2$

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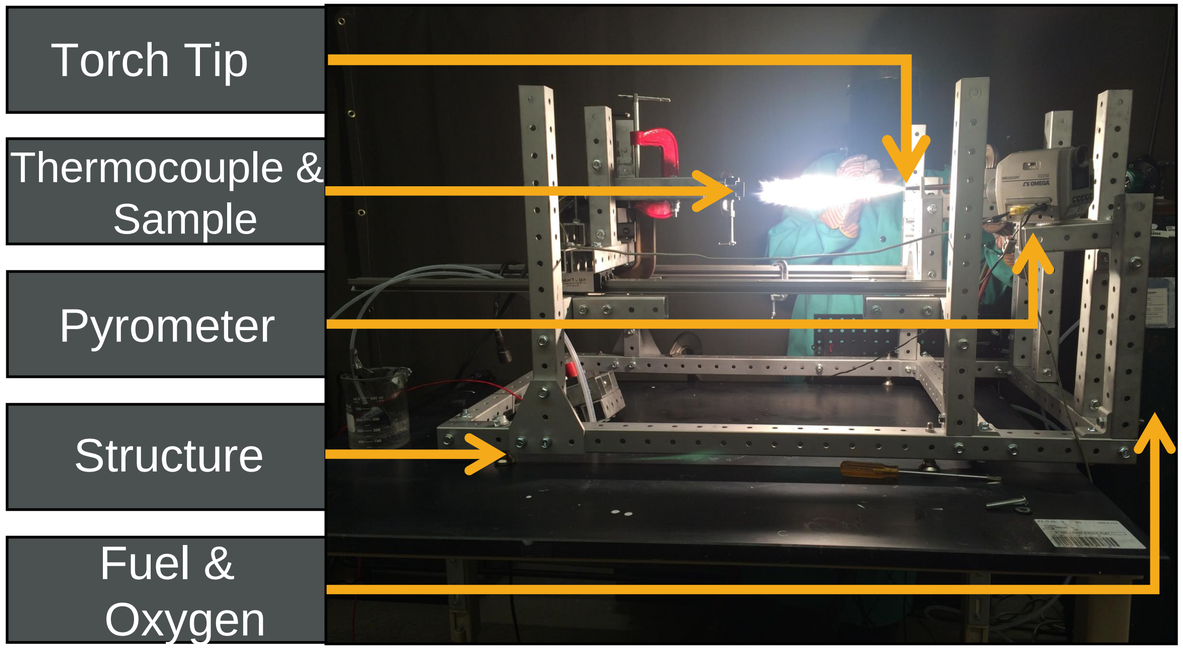
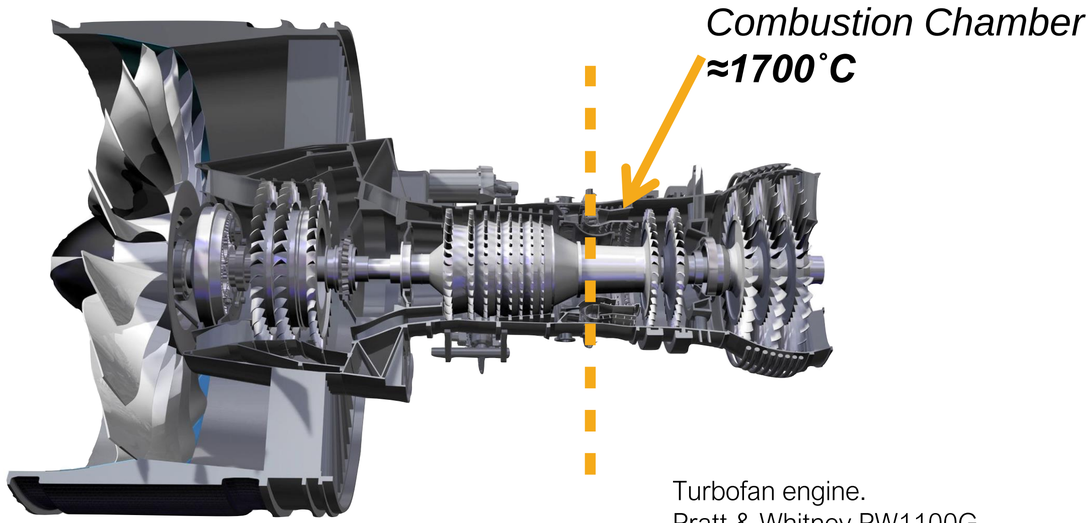
# Simulating The Interaction of Impurities In The Gas Turbine




Turbofan engine.
Pratt & Whitney PW1100G
**www.pw.utc.com**

- Full view of the sample as compared to a furnace.
- It is possible to measure the heat transfer.

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# YSZ TBC Hot Corrosion Study

## Control Sample

**APS Sample**

- Geometry: Squares of 1 in.
- TBC: 93%$ZrO_2$ -7%$Y_2O_3$ (Agglomerated & Sintered)
- Bond Coat: Ni(24-25)Cr(5.0-7.0)Al(0.3-0.5)Y

**SEM**

Microstructure for Reference.

**Ablation Rig**

- 4 Cycles of 2min ea.
- Temp: 1250°C -1300 °C

**SEM**

After Each Cycle

## Furnace Sample

**APS Sample**

Same as Control Sample

**Cocktail**

CMAS Composition

**Impurities Deposited**

1mg/cm$^2$

**Furnace**

- 1 Cycle of 4hrs.
- Temp:1250°C

**SEM**

- After Each Cycle

## Ablation Rig Sample

**APS Sample**

Same as Control Sample

**Cocktail**

CMAS Composition

**Impurities Deposited**

1mg/cm$^2$

**Ablation Rig**

- 4 Cycles of 2min ea.
- Temp: 1250°C -1300 °C

**SEM**

- After Each Cycle

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# Control Sample Ablation Rig Experiment

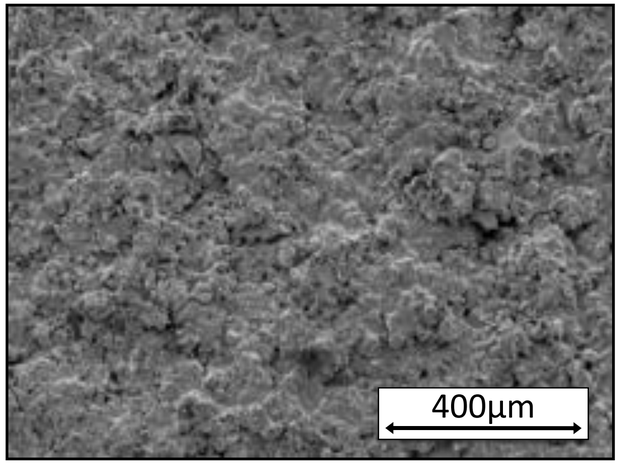
APS Sample

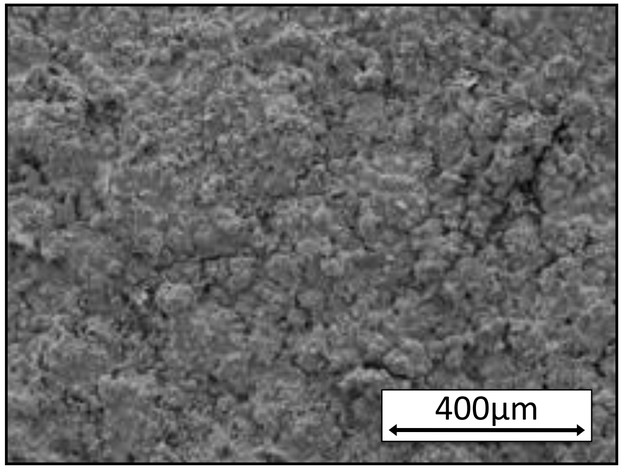
SEM (Reference)

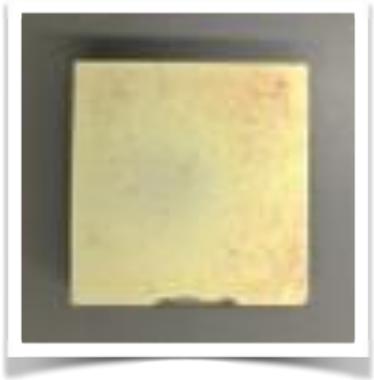
Ablation Rig
4 Cycles

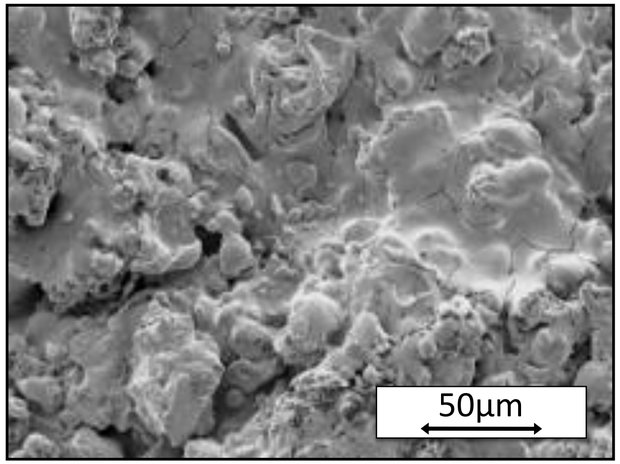
SEM (Last Cycle)

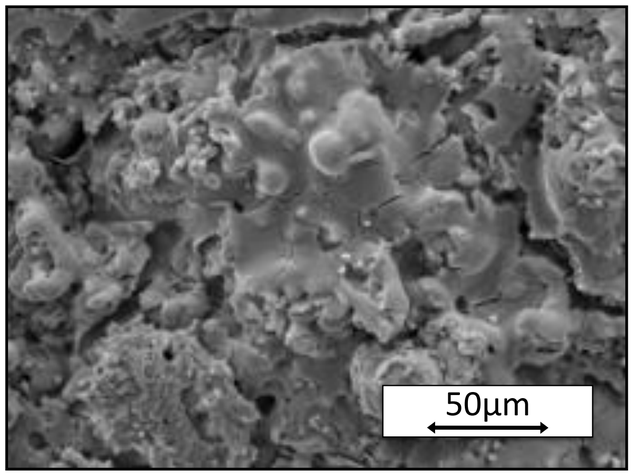
APS Sample
(After 4 Cycles)



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# Hot Corrosion Furnace Experiment

APS Sample

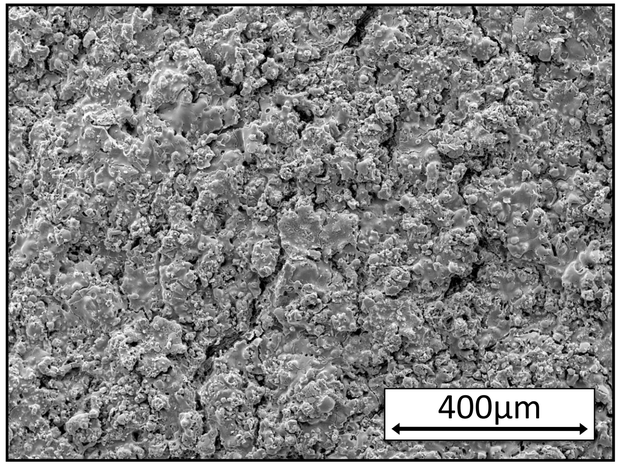
Impurities Deposited ($1 mg/cm^2$)

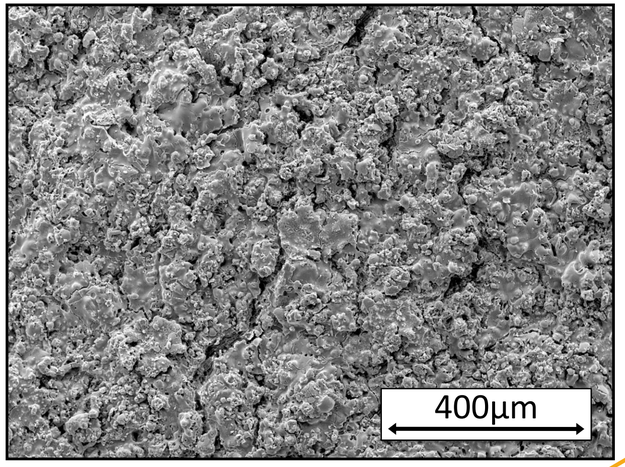
SEM (Reference)

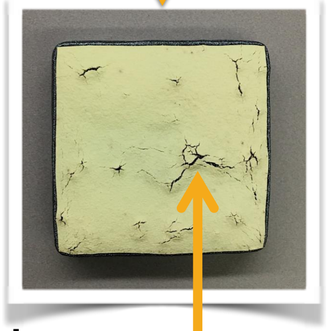
Furnace (1 Cycle)

SEM (After Furnace Cycle)

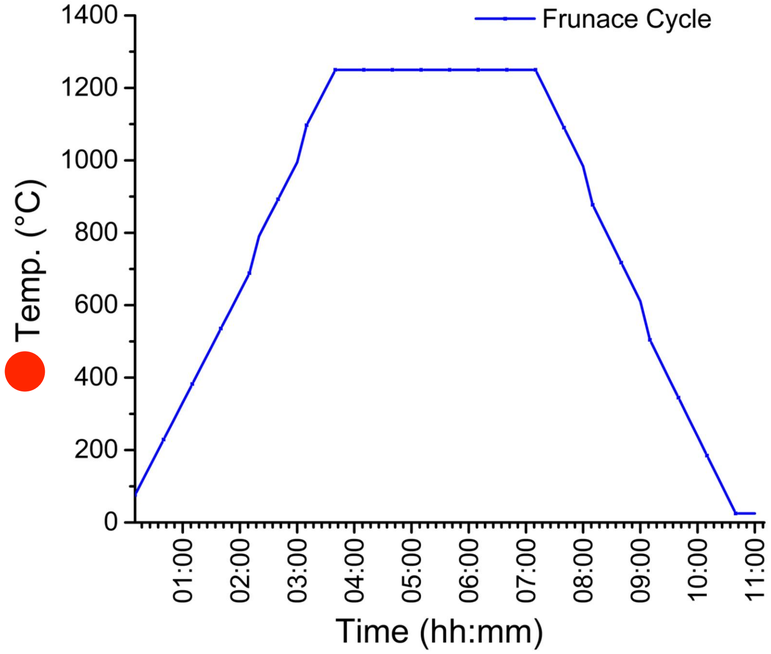
APS Sample (After Furnace Cycle)

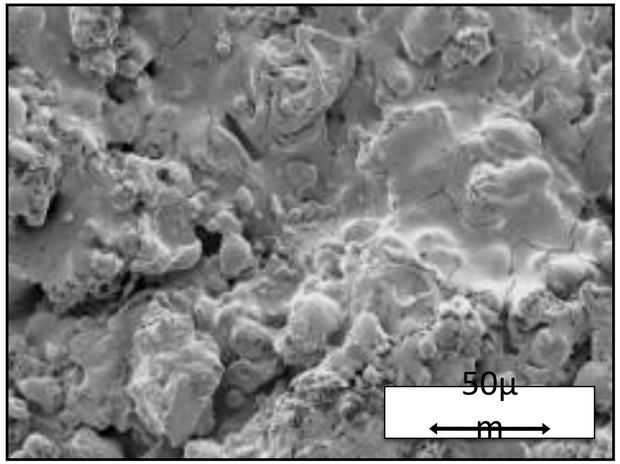


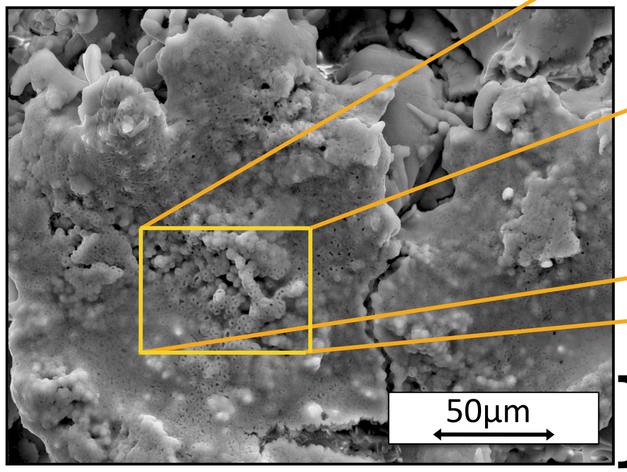



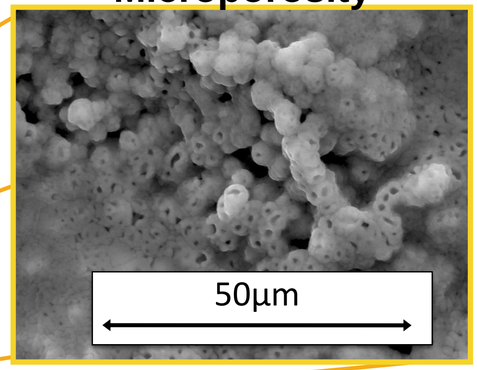
Crack




Microporosity

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# Hot Corrosion Ablation Rig Experiment

APS Sample

Impurities Deposited (1mg/cm$^2$)

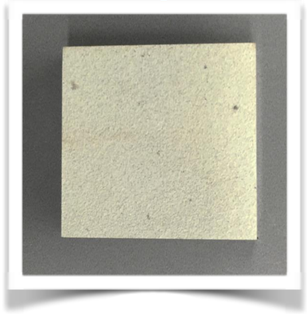
Ablation Rig 2 Cycles

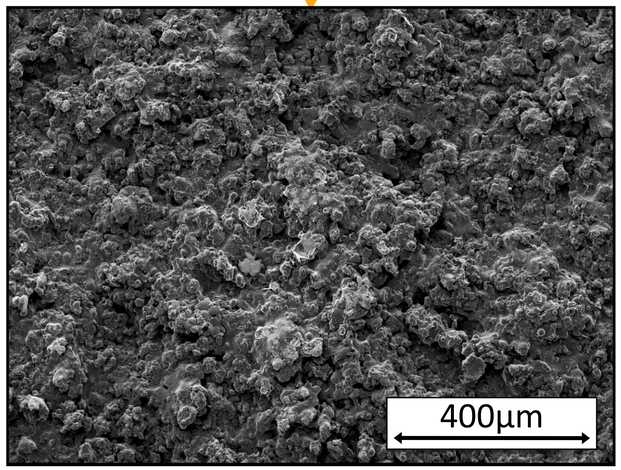
SEM (After 2 Cycles)

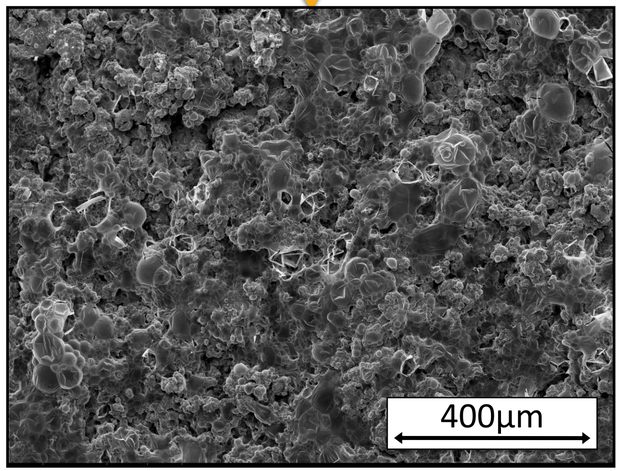
Ablation Rig (+2 Cycles)

SEM (After 2 Cycles)

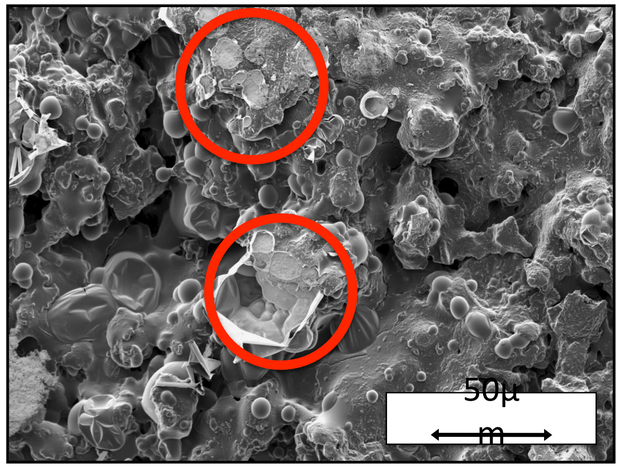
APS Sample (After 4 Cycles)

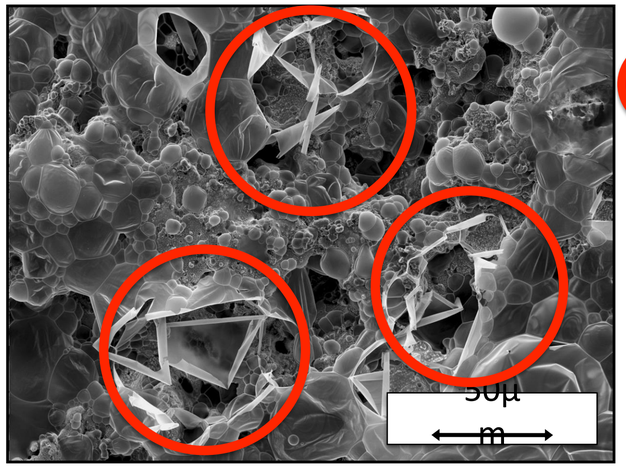





Delamination

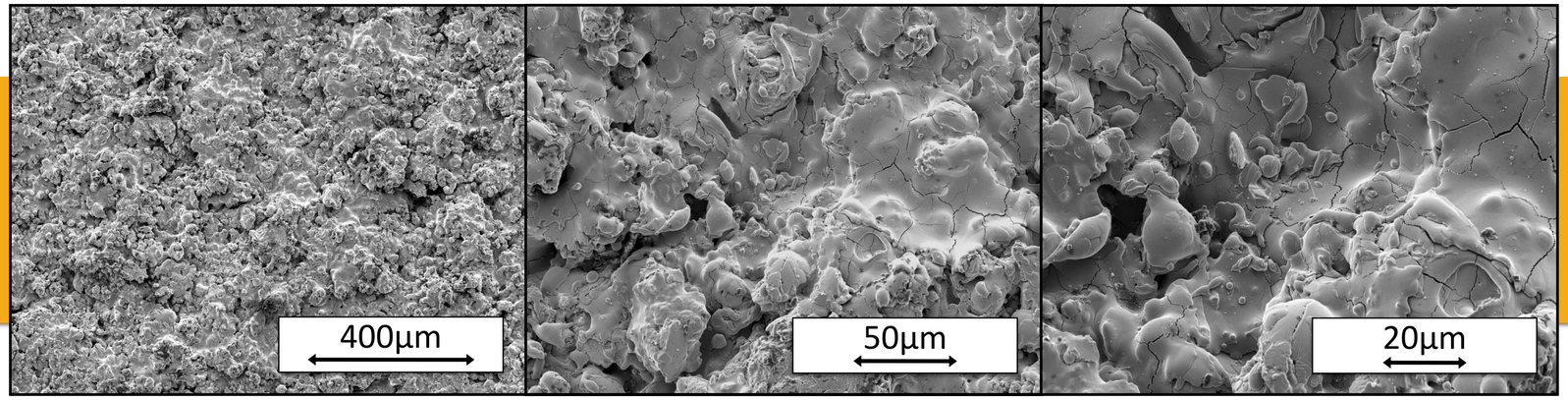



Microstructure Damage

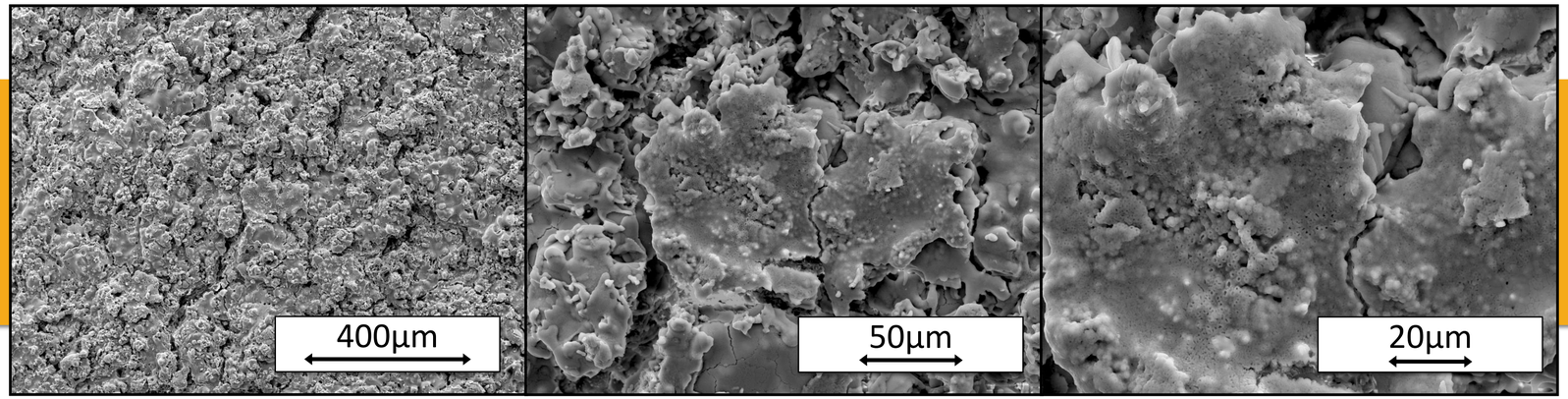
# Ca, Mg, Al, Si in Solution Greatly Hasten Failure of TBC Subject to Thermal Cycling

**Control Sample**



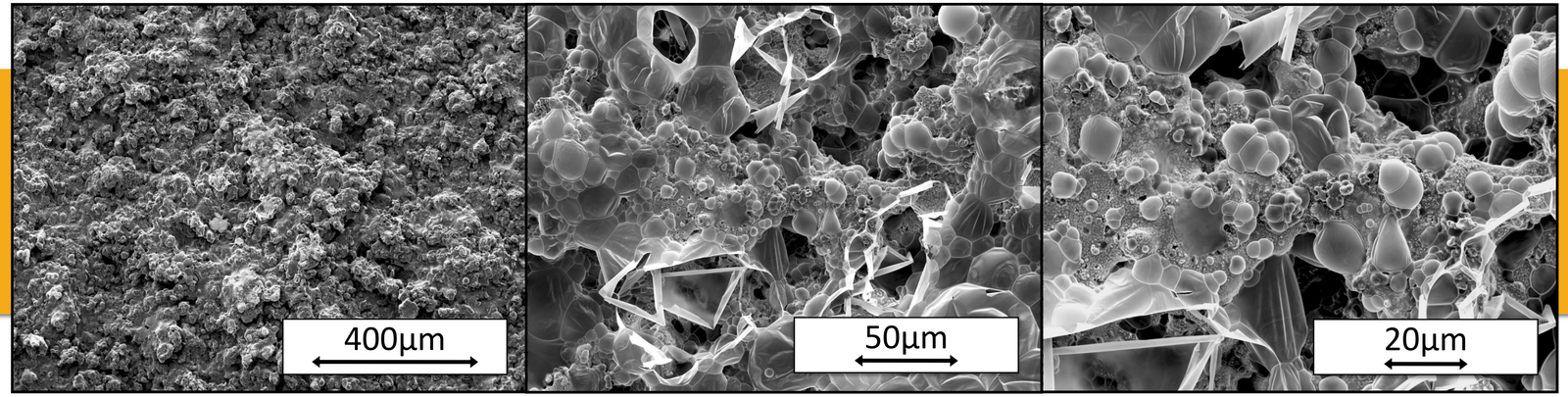

*No Changes*

**Furnace Sample**




- *Macroscopic Cracks*
- *Microporosity*

**Ablation Rig Sample**




- *Delimitation of TBC*
- *Microstructural Damage*

# Conclusions

- Due to the growing importance of biofuels worldwide, identification of the contaminants that will be found in biofuels and a specific understanding of the negative effects of these impurities its mandatory to avoid failure of gas turbines.

- Even though the chemical composition of biomass is simpler than that of fossil fuels, composition of biomass is highly variable and therefore different types of biofuel blends will have different detrimental effects on the TBC's.

- The implementation of the methodology explained before, will allow us to study the effect of different combinations of impurities on the TBC.

# THANK YOU FOR YOUR ATTENTION